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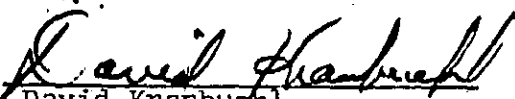
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Molecular Weight - Property Relationships
of High Performance Polymers Used
for Adhesives and Composites

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PROPERTY RELATIONSHIPS OF HIGH PERFORMANCE
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Abstract

Degradation of high performance polyimide precursor resins was investigated by measuring the molecular weight of the polymers in solution, using a membrane osmometer. It was found that polyimide precursor resins composed of BTDA and ODPA combined with DABP and MDA were unstable in DMAC.

The degradation rate was found to depend upon the chemical nature of the isomeric diamine and the geometric structure about the amide linkage. The polymers of DABP were less susceptible to degradation than those of MDA and *p,p'*-compounds were more stable than *m,m'*-compounds. These results suggest that degradation is correlated with the basicity of the diamine. That is, the rate of the degradation reaction increases with the basicity of the diamine group in the polyimide precursor resin.

The presence of water and a higher temperature increased the degradation rate of the polymers. A linear relationship between the degradation rate constant and water content was obtained in the concentration range studied. When the solution contained 1(v/v)% H₂O, the rate was three times greater than that of the anhydrous solution.

RESULTS AND DISCUSSION

1. Degradation of ODPA-m,m'-MDA

The result of molecular weight measurements made on a new polyimide polymer ODPA-m,m'-MDA is shown in Table VIII. The purpose of the measurements was to determine the size of the polymer and the extent to which chemically end-capping the polymer with phthalic anhydride or simply adding phthalic anhydride to the polymer solution retards degradation. The molecular weight of the polyimide polymer which was chemically end-capped was 17600 when measured on the same day the solution was prepared. The molecular weight of the non-end-capped polymer was 13300 when measured on the same day of the preparation. The change in molecular weight due to degradation of the polymer was observed as a function of time.

The experimental results show that the polyimide polymer is unstable in DMAC. Chemically end-capping the polymer (E-1) appears to have little effect on the initial rate of degradation (see Figure 3). The rate constant for the initial stage of degradation was $5.8 \times 10^{-3} \text{ day}^{-1}$. However, adding phthalic anhydride (1% of the weight of the polymer) to the DMAC solution (U-2) is a simple and effective step which appears to almost completely stop the degradation process. This may be attributed to the fact that the phthalic anhydride reacts with

TABLE VIII

Change in Molecular Weight Due to Polymer Degradation of
ODPA-m,m'-MDA at Room Temperature

Time Elapsed in Days, t	Molecular Weight of ODPA-m,m'-MDA*, \bar{M}_n		
	E-1	U-1	U-2
0	17600	12800	13300
1	17100	-	-
2	-	11700	-
7	14600	10800	-
14	-	11200	-
15	13800	-	-
20	-	10000	-
21	-	10200	-
47	-	-	12400
50	14200	-	-
68	-	-	12900
80	12900	-	-

* E-1: the end-capped polyimide polymer

U-1: the non-end-capped polyimide polymer

U-2: the non-end-capped polyimide polymer plus 1(w/w) %
phthalic anhydride

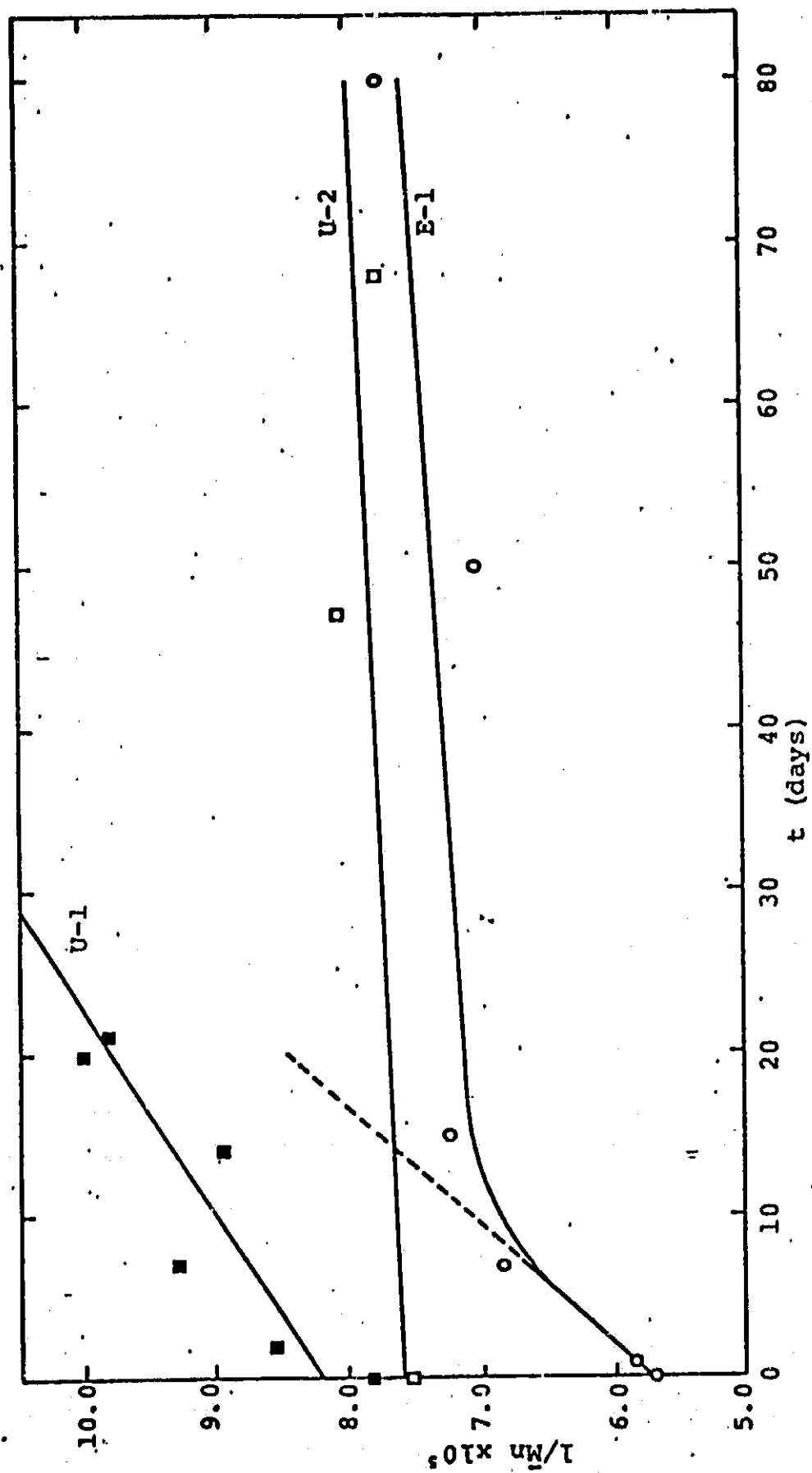


Figure 3. Change in molecular weight due to polymer degradation of ODPa-m,m'-MDA at room-temperature

the water present in the solvent DMAC, assuming that the presence of water accelerates degradation of the polymer. The degradation rate of the non-end-capped polymer without phthalic anhydride (U-1) was $3.5 \times 10^{-3} \text{ day}^{-1}$. Assuming that sample E-1 consisted of only end-capped polymers, the fact that the end-capped polymer degrades suggests that the C-N bonds along the chain backbone are susceptible to degradation and that degradation need not be initiated at the end groups of the polymer.

2. Degradation of a Series of BTDA polyimide Precursor Resins

Degradation rate as a function of the chemical nature and structure of diamines. The change in molecular weight due to degradation of polyimide precursor resins composed of BTDA combined with DABP and MDA was observed as a function of time (Table IX). It was found that the degradation rate k (day^{-1}) depended upon the nature of the isomeric diamines and the geometric structure about the amide linkage. The degradation rates calculated from the slope of the plot of $1/\bar{M}_n$ vs. t in Figure 4 were 19.8×10^{-3} for BTDA-*m,m'*-MDA, 12.8×10^{-3} for BTDA-*m,m'*-DABP, 9.9×10^{-3} for BTDA-*p,p'*-MDA, and 4.4×10^{-3} for BTDA-*p,p'*-DABP. The ratio of the k 's is 4.5 : 2.9 : 2.2 : 1 in the same order. Comparing the basicity of the diamines, the strongest is *m,m'*-MDA due to the effect of its electron-donating CH_2 group at the meta position and the weakest is *p,p'*-DABP due to its electron-withdrawing C=O group at the para position. The degradation rate was greatest with BTDA-*m,m'*-MDA and smallest with BTDA-*p,p'*-DABP. If the degradation

TABLE IX

Change in Molecular Weight Due to Degradation of Polyimide Precursor Resins at 27°C

Batch I

Time Elapsed in Days, t	BTDA-p, \bar{p}' -DABP $\bar{M}_n \cdot 1/\bar{M}_n \times 10^4$	BTDA-m, \bar{m}' -DABP $\bar{M}_n \cdot 1/\bar{M}_n \times 10^4$	BTDA-p, \bar{p}' -MDA $\bar{M}_n \cdot 1/\bar{M}_n \times 10^4$	BTDA-m, \bar{m}' -MDA $\bar{M}_n \cdot 1/\bar{M}_n \times 10^4$
0	9290	1.08	13470	14470
1	10040	0.996	-	-
2	-	-	12750	11890
3	10300	0.971	-	-
7	9250	1.08	10910	9280
14	8920	1.12	9560	7260
21	8210	1.22	8390	5800
28	7490	1.34	6820	-
slope ($k/\bar{M}_0 \times 10^4$)	0.011	0.032	0.024	0.048
intercept ($1/\bar{M}_n(0) \times 10^4$)	0.998	1.19	0.730	0.722
rate constant ($k \times 10^3$) (day ⁻¹)	4.4	12.8	9.9	19.8

TABLE IX - continued

Batch II

Time Elapsed in Days, t	BTDA-p,p'-DABP Mn	1/Mn x10 ⁴	BTDA-m,m'-MDA Mn	1/Mn x10 ⁴
0	9860	1.01	11200	0.893
3	10300	0.971	10100	0.990
6	-	-	9250	1.08
7	9430	1.06	-	-
11	-	-	8130	1.23
14	9280	1.08	7390	1.35
21	-	-	6330	1.58
22	8270	1.21	-	-
28	8360	1.20	5550	1.80
slope (k/M ₀ x10 ⁴)		0.0082		0.033
intercept (1/Mn(0) x10 ⁴)		0.987		0.876
rate constant (k x10 ³) (day ⁻¹)		3.3		13.6

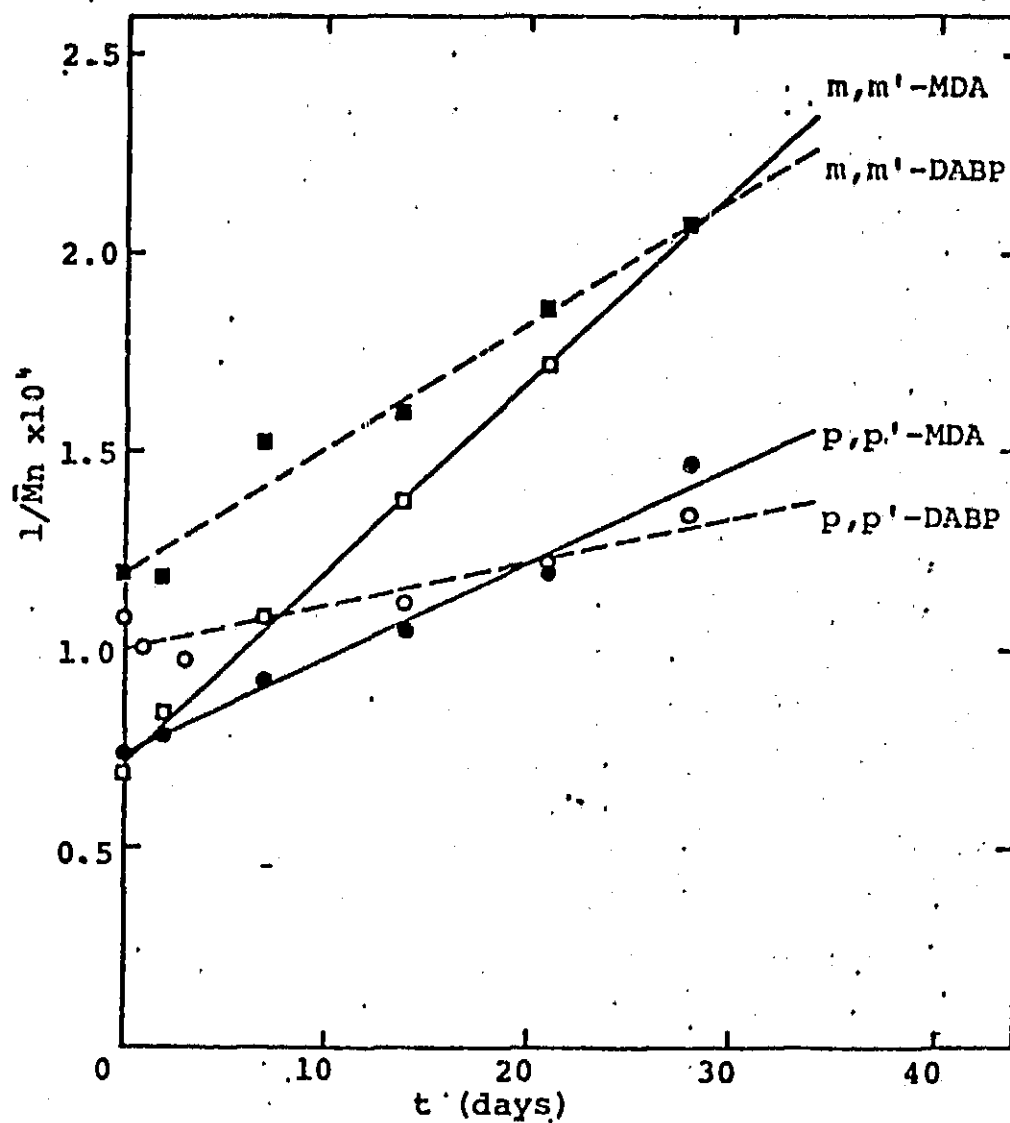


Figure 4. Change in molecular weight due to degradation of polyimide precursor resins as a function of time at 27°C

rate is correlated with the basicity of the diamine in such a manner that the more basic the diamine, the faster degradation occurs, then the following would be observed:

$k_{\text{MDA}} > k_{\text{DABP}}$ and $k_{\text{m,m'-compound}} > k_{\text{p,p'-compound}}$. From the data obtained, it can be seen that k is greater for the MDA polymers than for the DABP polymers: $k_{\text{p,p'-MDA}}/k_{\text{p,p'-DABP}}$ is 2.2 and $k_{\text{m,m'-MDA}}/k_{\text{m,m'-DABP}}$ is 1.5. It is also seen that the p,p'-compounds degrade less rapidly than the m,m'-compounds: $k_{\text{m,m'-DABP}}/k_{\text{p,p'-DABP}}$ is 2.9 and $k_{\text{m,m'-MDA}}/k_{\text{p,p'-MDA}}$ is 2.0. Thus, the degradation rate is correlated with the basicity of the diamines for polyimide precursor resins studied.

It has been reported ⁽¹⁾ that, in the preparation of polyimide polymers from isomeric diamines, the more basic the amine group, as a general rule, the more reactive it is toward other monomers, for example, aromatic dianhydrides. The result of the present study suggests that diamines which favor the polymerization reaction also favor degradation of the products.

Figures 5a and b and Table IX show the results of degradation studies on polymers from two different batches. The degradation rate of BTDA-p,p'-DABP (batch II) was 3.3×10^{-3} and that of BTDA-m,m'-MDA was 13.6×10^{-3} . Both of these values are somewhat lower than those for batch I. The uncertainty in k was estimated graphically from the error bars.³⁴ The results of the analysis are

(1)

P. R. Young and H. M. McNair, Anal. Chem., 47, 756 (1975).

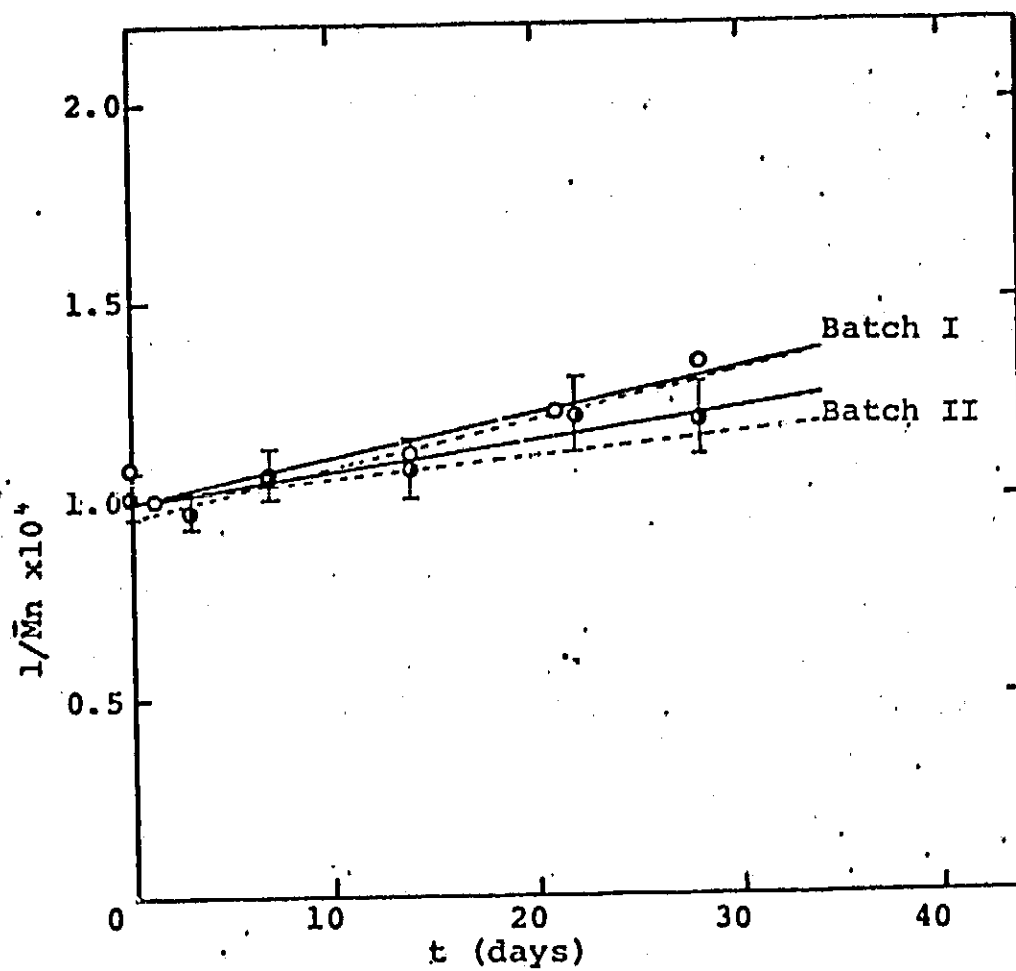


Figure 5a. The change in molecular weight due to degradation of BTDA-p,p'-DABP at 27°C

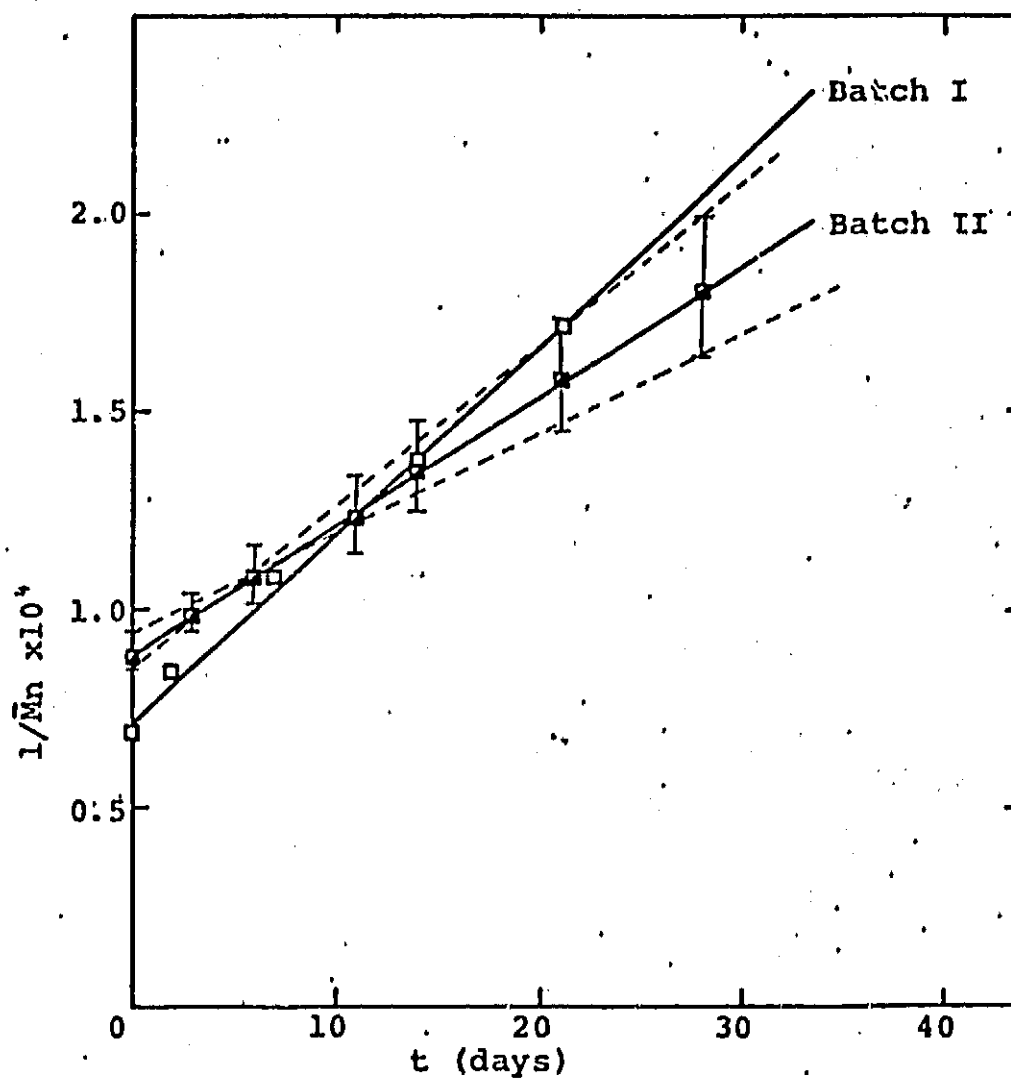


Figure 5b. The change in molecular weight due to degradation of BTDA-m,m'-MDA at 27°C

	$k \times 10^3$
BTDA-p,p'-DABP (batch I)	4.4 ± 1.0
BTDA-p,p'-DABP (batch II)	3.3 ± 1.0
BTDA-m,m'-MDA (batch I)	19.8 ± 4.0
BTDA-m,m'-MDA (batch II)	13.6 ± 3.0

The results suggest that there is a small effect of the polymerization conditions on the rate constant k . Variation in the amount of exposure to moisture during synthesis is a possible cause.

Water effect. The effect of the presence of water in the solvent DMAC on degradation of polyimide precursor resins was investigated and the results are shown in Table X and Figures 6a and b. The water content of anhydrous DMAC was checked by Hewlett-Packard 5700 Research Gas Chromatograph⁽²⁾ and was found to be less than 0.05%. In order to examine the water effect, 1(v/v)% of H₂O was added to the solvent when the polymer solutions were prepared. The degradation rates obtained were 12.8×10^{-3} for BTDA-p,p'-DABP (batch I) and 31.8×10^{-3} for BTDA-p,p'-MDA (batch I). These results show that the presence of water increased the degradation rates of BTDA-p,p'-DABP and BTDA-p,p'-MDA about three times (2.9 for BTDA-p,p'-DABP and 3.2 for BTDA-p,p'-MDA).

Table XI and Figure 7 show the results of a detailed investigation of the degradation of BTDA-m,m'-DABP (batch II)

(2) A 6' x 1/4" column packed with Porapak Q (80/100 mesh) was used for the separation of water from DMAC at 250°C. Porapak Q is prepared especially for good water-separation. A linear calibration curve for water content was obtained from the peak heights of water added to the solvent in the amounts of 0.1 and 1.0(v/v)% of the solvent.

TABLE X

Effect of Water on Degradation of Polyimide Precursor Resins
(Batch I) in DMAC Containing 1(v/v)% H₂O at 27°C

Time Elapsed in Days, t	BTDA-p,p'-DABP		BTDA-p,p'-MDA	
	Mn	1/Mn x10 ⁴	Mn	1/Mn x10 ⁴
0	8330	1.20	10800	0.926
3	8660	1.15	8020	1.25
7	7290	1.37	6020	1.66
14	6780	1.47	4970	2.01
22	5310	1.88	-	-
slope (k/M ₀ x10 ⁴)		0.032		0.077
intercept (1/Mn(0) x10 ⁴)		1.12		1.00
rate constant (k x10 ³) (day ⁻¹)		12.8		31.8

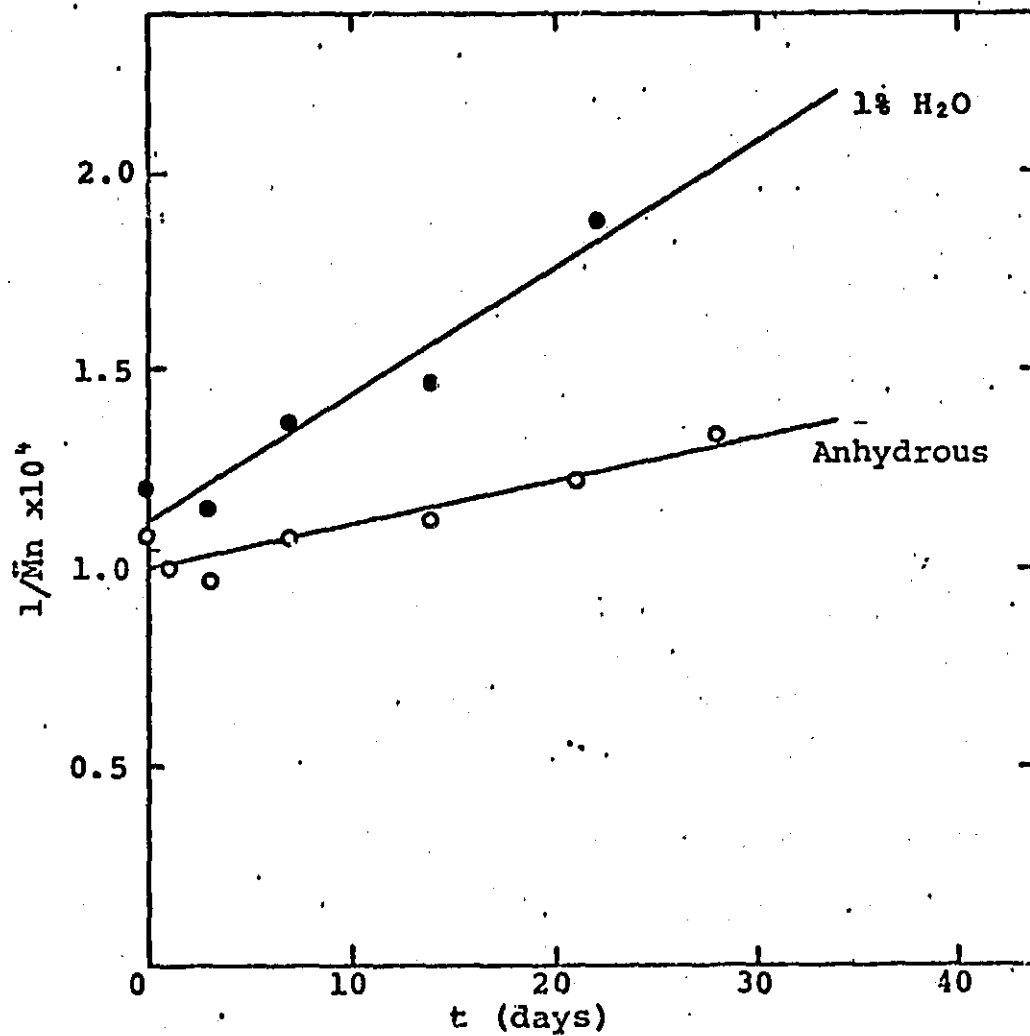


Figure 6a. Effect of water on degradation of BTDA-p,p'-DABP in DMAC containing 1(v/v)% H_2O at $27^\circ C$

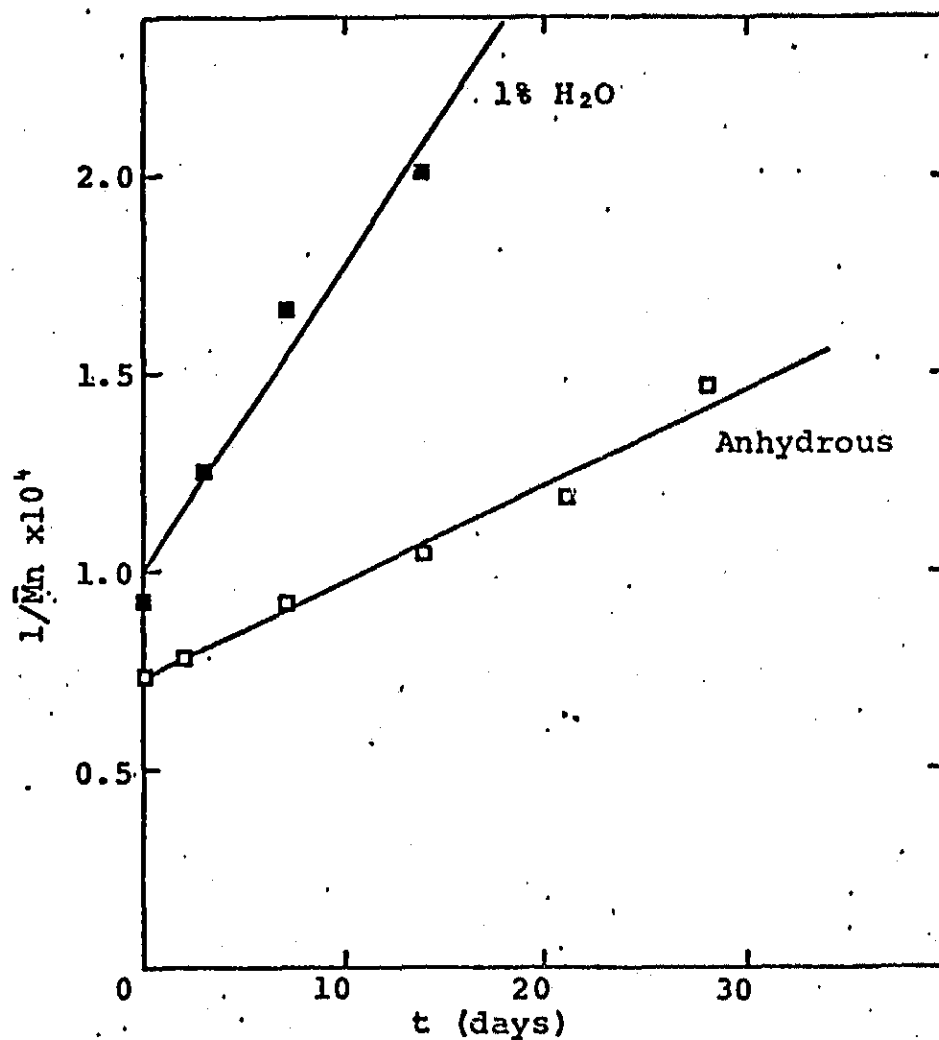


Figure 6b. Effect of water on degradation of BTDA-p,p'-MDA in DMAC containing 1(v/v)% H₂O at 27°C

TABLE XI

Effect of Water on Degradation of BTDA-m, m'-DABP (Batch II) at 27°C

Time Elapsed in Days, t	H ₂ O Content Mn	0.5% l/Mn x10 ⁴	Mn	0.3% l/Mn x10 ⁴	Mn	0.1% l/Mn x10 ⁴	<0.05% ¹⁾ Anhydrous ²⁾
0	9010	1.11	8590	1.16	10900	0.917	
2	8600	1.16	-	-	-	-	
3	-	-	8160	1.22	9550	1.05	
7	7140	1.40	6450	1.55	8270	1.21	
14	4870	2.05	5350	1.87	6860	1.46	
slope (k/M ₀ x10 ⁴)		0.068		0.053		0.038	0.032
intercept (l/Mn(0) x10 ⁴)		1.04		1.13		0.927	1.19
rate constant (k x10 ³)(day ⁻¹)		27.3		21.3		15.2	12.8
							12.2

1) result of Batch I

2) calculated from the graph of Figure 8

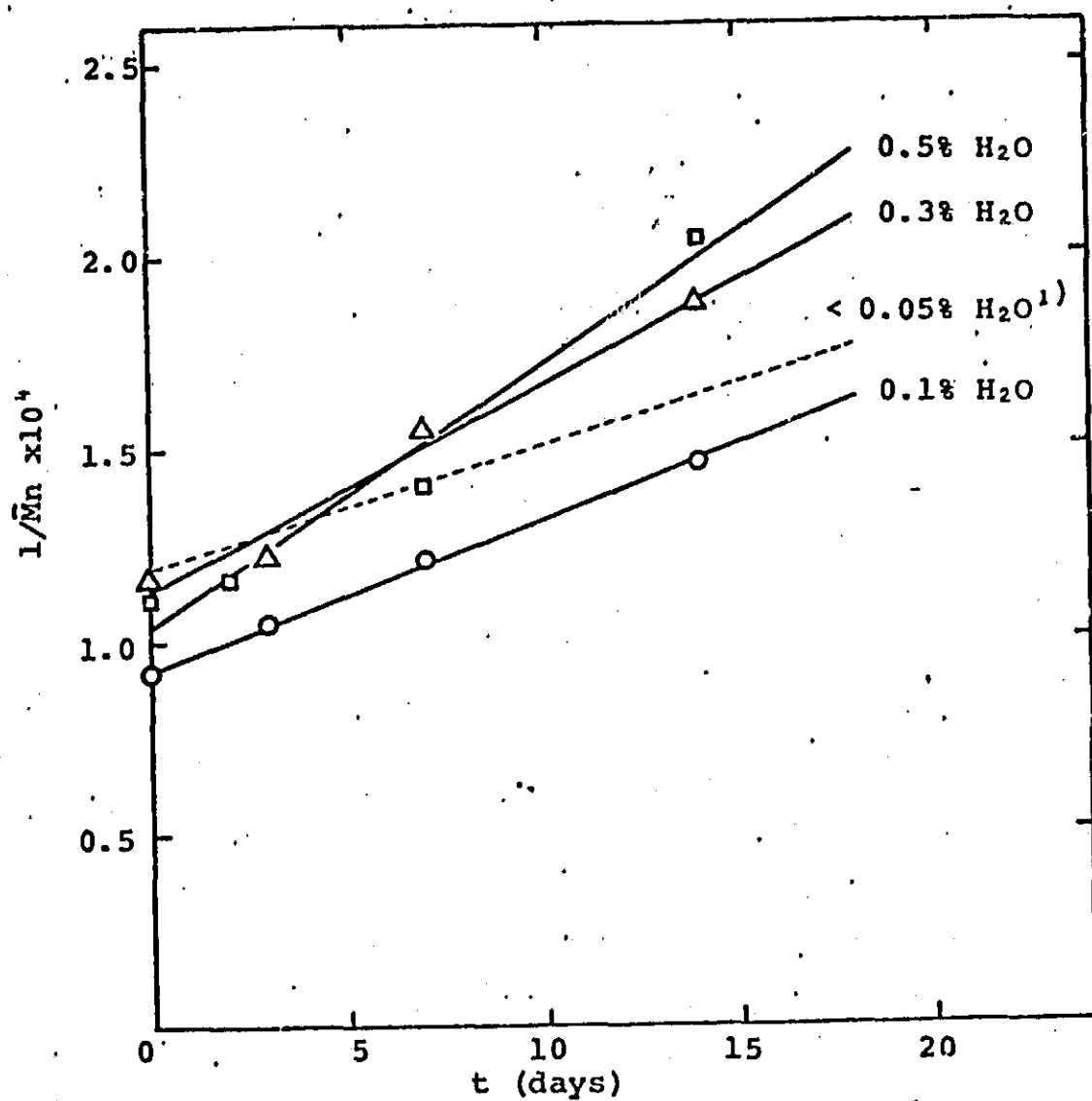


Figure 7. Effect of water on degradation of BTDA-m,m'-DABP (Batch II) at 27°C

1) result of Batch I

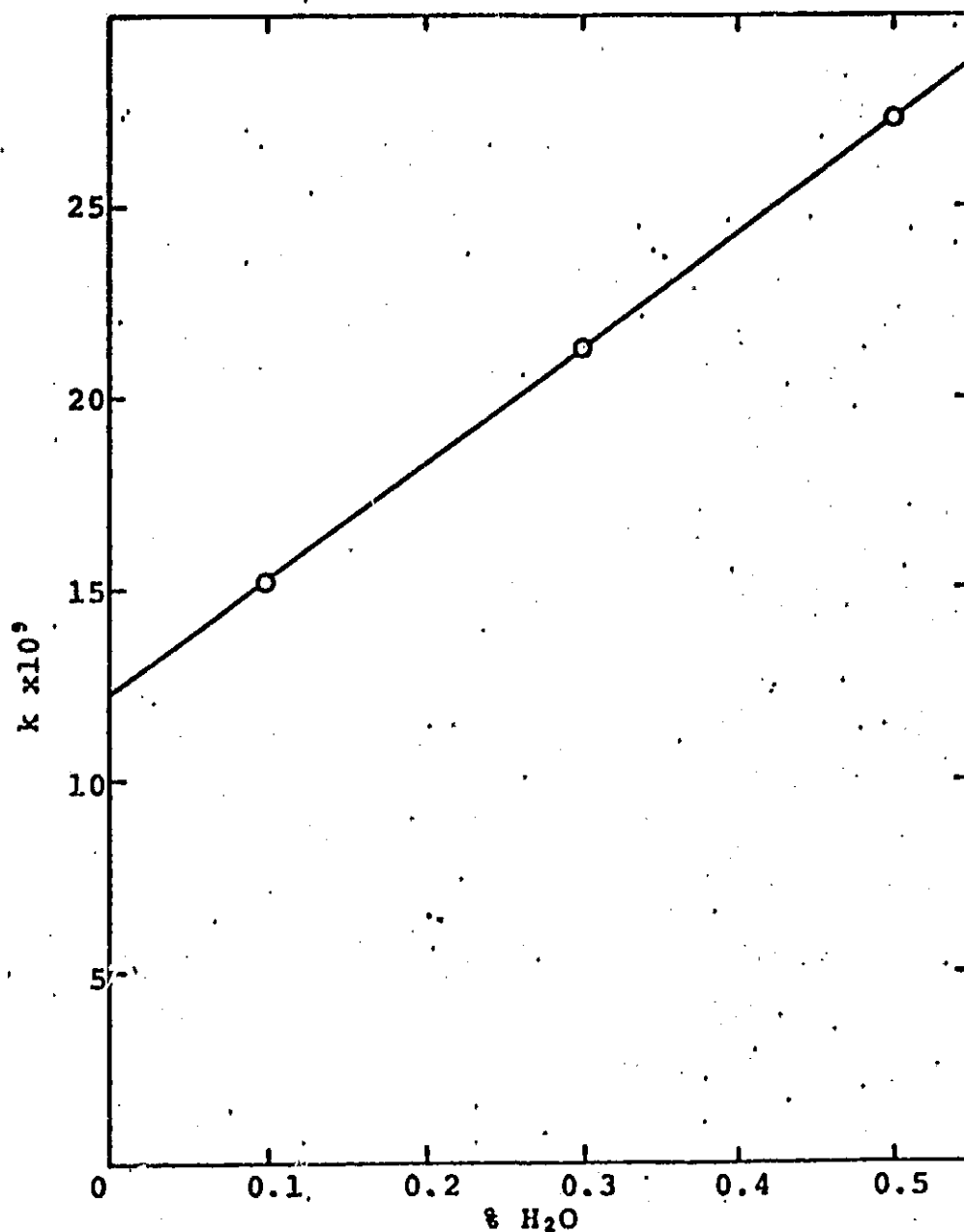


Figure 8. Plot of the degradation rate constant of BTDA-m,m'-DABP vs. the amount of water added to the solvent DMAC

in DMAC containing different amounts of water. Polymer solutions containing 0.1, 0.3, and 0.5(v/v)% H₂O were prepared by adding water to the solvent. The degradation rate increased with the larger amounts of water: $k_{0.1\%H_2O}$ was 15.2×10^{-3} ; $k_{0.3\%H_2O}$, 21.3×10^{-3} ; and $k_{0.5\%H_2O}$, 27.3×10^{-3} . In Figure 8 the degradation rate for each solution is plotted against the amount of water added. The observed linear relationship suggests that the degradation rate is proportional to the water content in the concentration range studied. From Figure 8 it can also be seen that the results are consistent with the rate constant, 12.8×10^{-3} , obtained for BTDA-m,m'-DABP of batch I in anhydrous DMAC containing less than 0.05% of water.

TABLE XII

Effect of Temperature on Degradation of BTDA-p,p'-DABP (Batch II)

Time Elapsed in Days, t	Temp.	27°C*		37°C	
		\bar{M}_n	$1/\bar{M}_n \times 10^4$	\bar{M}_n	$1/\bar{M}_n \times 10^4$
0		9860	1.01	9730	1.03
1		-	-	9180	1.09
3		10300	0.971	7920	1.26
5		-	-	7620	1.31
7		9430	1.06	-	-
11		-	-	5080	1.97
14		9280	1.08	-	-
22		8270	1.21	-	-
28		8360	1.20	-	-
slope					
(k/M ₀ × 10 ⁴)			0.0082		0.0849
intercept					
(1/M _n (0) × 10 ⁴)			0.987		0.993
rate constant					
(k × 10 ³) (day ⁻¹)			3.3		34.1

* the same result in Table IX

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